EPR Study of Vanadium Oxide Bis(8-quinolinolate) Doped in Zinc Bis(8-quinolinolate) Dihydrate

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Note

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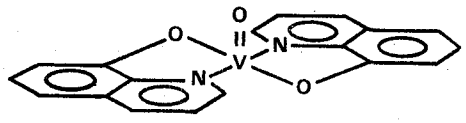
EPR signal of vanadium oxide bis(8-quinolinolate), $[VO(quin)_2]$, has been observed in the matrix of zinc bis(8-quinolinolate) dihydrate, $[Zn(quin)_2(H_2O)_2]$. EPR parameters of $VO(quin)_2$ in $Zn(quin)_2(H_2O)_2$ have been found to be similar to those of $VO(quin)_2$ in toluene. The results indicate that $VO(quin)_2$ doped in $Zn(quin)_2(H_2O)_2$ has no ligand H_2O to interact at the axial position.

KEY WORDS: Magnetic properties / EPR parameters / Axial interaction /

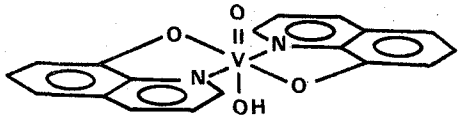
INTRODUCTION

Vanadium oxide bis(8-quinolinolate), $[VO(quin)_2]$, [1], is generally unstable in air, and is rapidly oxidized to diamagnetic hydroxo (oxo)(8-quinolinolate) vanadium, $[VO(OH)(quin)_2]$, [2]. In the matrix of zinc bis(8-quinolinolate) dihydrate, $[Zn(quin)_2(H_2O)_2]$, [3], $VO(quin)_2$ is expected to be embedded because of the similar molecular shape. When $VO(quin)_2$ is embedded in the matrix, the following three possibilities can be considered.

1) $VO(quin)_2$ is oxidized to $VO(OH)(quin)_2$ by the reaction with H_2O.
2) $VO(quin)_2$ hydrates and becomes $VO(quin)_2(H_2O)$, [4].
3) $VO(quin)_2$ exists stable without distinct interactions with the matrix.



[1]



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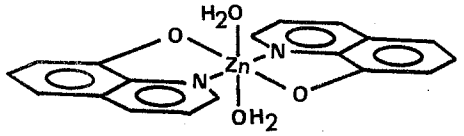

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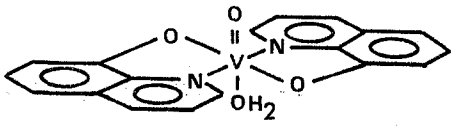

[4]

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In the first case no EPR spectrum can be observed because vanadyl ion becomes diamagnetic by the conjugation with OH^-. In the second case EPR parameters should be observed with some modifications as a result of the axial interaction between VO^{2+} and a ligand H_2O. In the last case EPR parameters should be similar to $VO(quin)_2$ in the solvent such as toluene which has no axial interation.

The structure of $VO(quin)_2$ doped in $Zn(quin)_2(H_2O)_2$ was determined from the above mentioned viewpoints.

EXPERIMENTAL

Preparation. $VO(quin)_2$ in $Zn(quin)_2(H_2O)_2$ was prepared by adding the aqueous solution of the mixture of $VOCl_2$ (5%) and $ZnSO_4 \cdot 7H_2O$ (95%) to an ethanolic solution of 8-quinolinol, and obtained as powdered precipitate. A toluene solution of $Cu(quin)_2$ (5%) was prepared by dissolving a powder of $Cu(quin)_2$ into pure toluene, where the powder had been obtained by mixing an aqueous solution of $CuSO_4 \cdot 5H_2O$ and ethanolic solution of 8-quinolinol.

Measurements. The X-band EPR spectra were measured with JES-ME-3X spectrometer using 100 KHz magnetic field modulation. The calibration of the field strength was made with Mn^{2+} doped in MgO.

RESULTS AND DISCUSSION

The EPR spectrum of $VO(quin)_2$ embedded in $Zn(quin)_2(H_2O)_2$ was obtained at room temperature as shown in Fig. 1. This indicates that $VO(quin)_2$ does not change into diamagnetic $VO(OH)(quin)_2$ even in this hydrated host crystal. The EPR parameters of $VO(quin)_2$ in $Zn(quin)_2(H_2O)_2$ were calculated using the following spin Hamiltonian with an axial symmetry.

$$H_s = \beta[g_{//} H_z S_z + g_\perp (H_x S_x + H_y S_y] + A_{//} I_z S_z + A_\perp (I_x S_x + I_y S_y), \qquad (1)$$

where $A_{//}$ and $A_\perp$ are the vanadium nuclear hyperfine constants.

From the Bleaney's second-order perturbation theory[1], the magnetic field at which the resonance occurs is given as below.

$$H_{\pm M_I} = \frac{g_0}{g}\left\{h\nu - AM_I - \frac{A_\perp}{4H_0}\left(\frac{A_{//}^2 + A_\perp^2}{A^2}\right)[I(I+1) - M_I^2]\right\}, \qquad (2)$$

where

$$g = (g_{//}^2 \cos^2\theta + g_\perp^2 \sin^2\theta)^{1/2}$$

and

$$A = (A_{//}^2 g_{//}^2 \cos^2\theta + A_\perp^2 g_\perp^2 \sin^2\theta)^{1/2}/g$$

The final EPR parameters were calculated by the least-square method. The spectra of $Cu(quin)_2$ in toluene were measured as shown in Fig. 2 for comparison. These

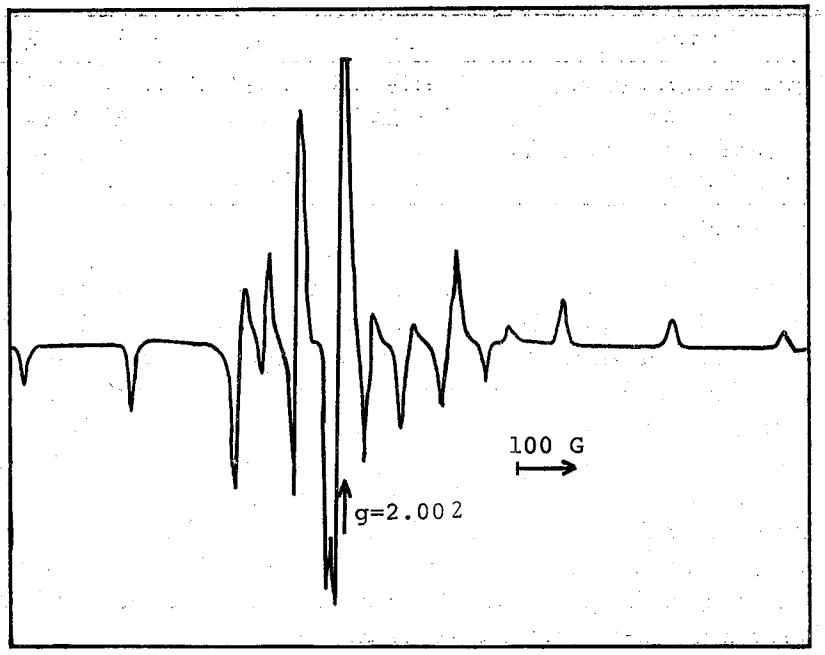

Fig. 1. The EPR spectrum of $VO(quin)_2$ in $Zn(quin)_2(H_2O)_2$ at room temperature.

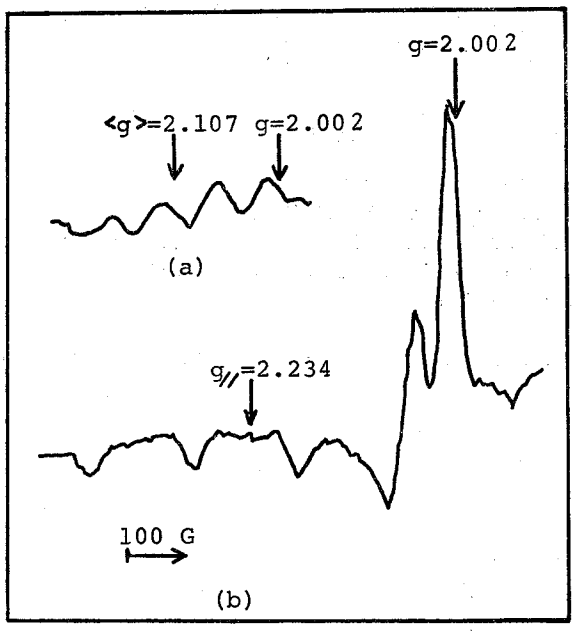

Fig. 2. The EPR spectra of $Cu(quin)_2$ in toluene at room temperature (a) and 77° K (b).

Table I. EPR parameters of $VO(quin)_2$ and $Cu(quin)_2$

Compound	$g_{//}$	$g_{\perp}$	$A_{//}(G)$	$A_{\perp}(G)$	Ref.
$VO(quin)_2$ in $Zn(quin)_2(H_2O)_2$	1.950±0.002	1.980±0.001	166±2	57±1	*
$VO(quin)_2$ in toluene	1.946±0.003	1.980±0.003	174±2	60±2	2)
$Cu(quin)_2(H_2O)_2$ in $Zn(quin)_2(H_2O)_2$	2.287	2.066	−160	−31	3)
$Cu(quin)_2$ in toluene	2.234	2.044	−170	−53	*

*: This work

EPR parameters obtained are listed in Table I, together with the values of $VO(quin)_2$ in toluene and $Cu(quin)_2(H_2O)_2$ in $Zn(quin)_2(H_2O)_2$ reported in Ref. 2 and Ref. 3 respectively. It is well known that for copper complexes EPR parameters are very sensitive to a matrix. When interacrtion between copper atom and the axial ligand is strong, the g value increases while $|A|$ value decreases.[3~7] The differences between g values of $VO(quin)_2$ in $Zn(quin_2\ (H_2O)_2$ and those of $VO(quin)_2$ in toluene are not significant. The differences in EPR parameters of $VO(quin)_2$ in those matrices are smaller than those of $Cu(quin)_2$. This means that the spin state of $VO(quin)_2$ is not affected so strong as in the case of $Cu(quin)_2$ by a matrix at the axial position in $Zn(quin)_2(H_2O)_2$. Therefore it is concluded that $VO(quin)_2$ has no ligand H_2O molecule at the axial position.

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